Ionel Haiduc,
Frank T. Edelmann

Supramolecular Organometallic Chemistry

WILEY-VCH

Weinheim New York Chichester
Brisbane Singapore Toronto

Table of Contents

1 Basic Concepts and Principles 1
1.1 Definitions 1
1.1.1 Supramolecular chemistry 1
1.1.2 Molecular recognition and host–guest interactions 3
1.1.3 Self-assembly and self-organization 4
1.2 Intermolecular Bond Types in Organometallic Supramolecular Systems 9
1.2.1 Dative bonding (electron-pair donor–acceptor bonding or Lewis acid–base interactions) 9
1.2.2 The secondary bond concept 14
1.2.3 Hydrogen-bond interactions 18
1.2.4 Ionic interactions 20
1.2.5 π-Bonding interactions 22

2 Molecular Recognition and Host–Guest Interactions 27
2.1 Organometallic Receptors and their Host–Guest Complexes 27
2.1.1 Organomercury macrocyclic receptors 27
2.1.2 Organocopper and organosilver potential receptors 29
2.1.3 Organocyclosiloxane receptors 29
2.1.4 Organotin macrocyclic receptors 35
2.1.5 Ferrocene-containing coronands and cryptands 37
2.1.5.1 Ferrocene polyoxa coronands 37
2.1.5.2 Ferrocene polyaza–oxa coronands and cryptands 40
2.1.5.3 Ferrocene polyaza coronands and cryptands 45
2.1.5.4 Ferrocene polyoxa-thia coronands 48
2.1.5.5 Ferrocene polythia coronands 49
2.1.5.6 Non-cyclic ferrocene receptors 50
2.1.6 Cobaltocenium receptors 52
2.1.7 Other metallocene receptors 56
2.1.8 Calixarene receptors modified with organometallic groups 58
2.1.9 Organometallic cyclotriveratrylene receptors 64

2.2 Organometallic Guests 65
2.2.1 Organometallic guests in inorganic hosts 65
2.2.1.1 Organometallics in zeolites and mesoporous silica 65
2.2.1.2 Organometallic compounds in layered chalcogenides, oxohalides, and oxides 68
2.2.2 Organometallic guests in organic hosts 70
2.2.2.1 Organometallic complexes of crown ethers, cryptands and related receptors 70
2.2.2.2 Organometallic molecules in cyclodextrin receptors 76
2.2.2.3 Organometallics in the thiourea lattice host 78

3 Supramolecular Self-Assembly by Dative Bonding (Electron-Pair Donor–Acceptor or Lewis Acid–Base Interactions) 95
3.1 Group 12 Metals – Zinc, Cadmium, Mercury 95
3.1.1 Self-assembly of organozinc compounds 95
3.1.1.1 Organozinc halides 95
3.1.1.2 Organozinc–oxygen compounds 96
3.1.1.3 Organozinc–sulfur compounds 100
3.1.1.4 Organozinc–selenium compounds 102
3.1.1.5 Organozinc–nitrogen compounds 103
3.1.2 Self-assembly of organocadmium compounds 104
3.1.3 Self-assembly of organomercury compounds 106
3.2 Group 13 Metals – Aluminum, Gallium, Indium, Thallium 107
3.2.1 Self-assembly of organoaluminum compounds 108
3.2.1.1 Organoaluminum halides 108
3.2.1.2 Organoaluminum–oxygen derivatives 109
3.2.1.3 Organoaluminum–sulfur derivatives 114
3.2.1.4 Organoaluminum–selenium and tellurium derivatives 116
3.2.1.5 Organoaluminum–nitrogen compounds 116
3.2.1.6 Organoaluminum–phosphorus and organoaluminum–arsenic compounds 122
3.2.2 Self-assembly of organogallium compounds 123
3.2.2.1 Organogallium halides 123
3.2.2.2 Organogallium–oxygen compounds 124
3.2.2.3 Organogallium–sulfur compounds 126
3.2.2.4 Organogallium–selenium and –tellurium compounds 127
3.2.2.5 Organogallium–nitrogen compounds 128
3.2.2.6 Organogallium–phosphorus, –arsenic and –antimony compounds 131
3.2.3 Self-assembly of organoindium compounds 133
3.2.3.1 Organoindium–halogen derivatives 134
3.2.3.2 Organoindium–oxygen derivatives 135
3.2.3.3 Organoindium–sulfur and –selenium compounds 136
3.2.3.4 Organoindium–nitrogen derivatives 137

3.2.3.5 Organoindium–phosphorus and –arsenic derivatives 139
3.2.4 Self-assembly of organothallium compounds 141
3.3 Group 14 Metals – Tin and Lead 146
3.3.1 Self-assembly of organotin compounds 146
3.3.1.1 Organotin halides 146
3.3.1.2 Dimeric organodistannoxanes $[XR_2SnOSnR_2X]_2$ and related compounds 148
3.3.1.3 Organotin hydroxides, alkoxides, and related compounds 150
3.3.1.4 Organotin carboxylates 156
3.3.1.5 Monoorganotin oxo-carboxylates 168
3.3.1.6 Organotin derivatives of inorganic acids 171

4 Supramolecular Self-Assembly by Formation of Secondary Bonds 195
4.1 Homoatomic Interactions 195
4.2 Group 12 Metals – Zinc, Cadmium, Mercury 202
4.2.1 Self-assembly of organomercury compounds 202
4.2.1.1 Organomercury halides 202
4.2.1.2 Organomercury–oxygen compounds 205
4.2.1.3 Organomercury–sulfur compounds 209
4.2.1.4 Organomercury–nitrogen compounds 212
4.3 Group 13 Metals – Gallium, Indium, Thallium 213
4.3.1 Self-assembly of organogallium compounds 213
4.3.2 Self-assembly of organoindium compounds 214
4.3.2.1 Organoindium halides 214
4.3.2.2 Organoindium–oxygen derivatives 216
4.3.2.3 Organoindium–nitrogen derivatives 217
4.3.3 Self-assembly of organothallium compounds 218
4.3.3.1 Organothallium halides 218
4.3.3.2 Organothallium–sulfur compounds 220
4.3.3.3 Organothallium–nitrogen compounds 224
4.4 Group 14 – Tin and Lead 227
4.4.1 Self-assembly of organotin compounds 227
4.4.1.1 Organotin halides 227
4.4.1.2 Organotin–oxygen compounds 234
4.4.1.3 Organotin–sulfur compounds 244
4.4.1.4 Organotin–nitrogen compounds 249
4.4.2 Self-assembly in organolead compounds 259
4.5 Group 15 – Arsenic, Antimony, Bismuth 265
4.5.1 Self-assembly in organoarsenic compounds 265
4.5.2 Self-assembly in organoantimony compounds 268
4.5.2.1 Organoantimony halides 268
4.5.2.2 Organoantimony–oxygen compounds 274
4.5.2.3 Organoantimony–sulfur compounds 276
4.5.2.4 Organoantimony–nitrogen compounds 282

4.5.3 Self-assembly in organobismuth compounds 282
4.5.3.1 Organobismuth–halogen compounds 282
4.5.3.2 Organobismuth–oxygen compounds 287
4.5.3.3 Organobismuth–sulfur compounds 288
4.5.3.4 Organobismuth–nitrogen compounds 290
4.6 Group 16 – Selenium and Tellurium 290
4.6.1 Self-assembly in organoselenium compounds 290
4.6.2 Self-assembly in organotellurium compounds 293
4.6.2.1 Organotellurium–halogen compounds 293
4.6.2.2 Organotellurium–oxygen compounds 298
4.6.2.3 Organotellurium–sulfur compounds 299
4.6.2.4 Organotellurium–nitrogen compounds 301

5 Supramolecular Self-Assembly by Hydrogen-Bond Interactions 319
5.1 Introduction 319
5.2 Group 14 Elements – Si, Ge, Sn, Pb 319
5.2.1 Organosilanols and organosiloxanols 319
5.2.2 Organogermanium hydroxides 327
5.2.3 Organotin compounds 328
5.3 Group 15 Elements – As, Sb, Bi 333
5.3.1 Organoarsenic compounds 333
5.3.2 Organoantimony compounds 335
5.4 Transition Metals (Organometallic Crystal Engineering) 337
5.4.1 Peripheral hydrogen-bonding 338
5.4.1.1 O–H···O hydrogen bonds involving carboxyl groups 338
5.4.1.2 O–H···O hydrogen bonds involving hydroxyl groups 342
5.4.1.3 N–H···O hydrogen bonds involving amido groups 352
5.4.1.4 C–H···O hydrogen bonds involving carbonyl ligands 352
5.4.2 Hydrogen bonds involving transition metal atoms 357
5.4.2.1 M–H···O≡C intermolecular hydrogen bonds 358
5.4.3 Hydrogen-bonds assisted by ionic interactions 359

6 Supramolecular Self-Assembly Caused by Ionic Interactions 371
6.1 Alkali Metals 371
6.1.1 Hydrocarbyls 371
6.1.1.1 Base-free alkali metal hydrocarbyls 373
6.1.1.2 Solvated alkali metal hydrocarbyls 377
6.1.2 Amides and related compounds 386
6.1.2.1 Amides and related nitrogen derivatives 387
6.1.2.2 Phosphides and arsenides 398
6.1.3 Alkoxides and their higher homologs 402
6.2 Alkaline Earth Metals 415

7 Supramolecular Self-Assembly as a Result of π-Interactions 425
7.1 Introduction 425
7.2 Main Group Elements 425
7.2.1 π-Interactions with acetylenes and allyl ligands 425
7.2.2 Cyclopentadienyl, indenyl, and fluorenyl complexes 426
7.2.3 Five-membered heterocycles 441
7.2.4 π-Interactions with arene rings 441
7.3 Transition Elements 452
7.3.1 Olefin complexes 452
7.3.2 Cyclopentadienyl complexes 452
7.3.3 Arene complexes 454
7.4 *f*-Elements 455
7.4.1 Acetylide complexes 456
7.4.2 Cyclopentadienyl complexes 456
7.4.3 Five-membered heterocycles 461
7.4.4 Arene complexes 462

Subject Index 469